CORROSION INHIBITION OF *AQUILARIA* METHANOLIC LEAF EXTRACTS FOR MILD STEEL IN HYDROCHLORIC ACID SOLUTION

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By

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Helen Lee Yun Sin

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LIST OF ABBREVIATIONS

AC	Alternating current
Ade	Adenosine
AMB	*Aquilaria malaccensis* (before inoculation)
CR	Corrosion rate
CPE	Constant phase element
EDX	Energy dispersive X-ray
EIS	Electrochemical impedance spectroscopy
FTIR	Fourier transform infrared
HCl	Hydrochloric acid
HOMO	Highest occupied molecular orbital
HPLC	High performance liquid chromatography
LOQ	Limit of quantification
LUMO	Lowest unoccupied molecular orbital
Inhi	Inhibitor
MS	Mass spectrometry
MS/MS	Tandem mass spectrometry
Q-TOF LC/MS	Quadrupole-time of flight liquid chromatography/mass spectrometry
RSD	Relative standard deviation
SCE	Saturated calomel electrode
SD	Standard deviation
SEM	Scanning electron microscope

SIB	*Aquilaria subintegra* (before inoculation)
SIC	*Aquilaria subintegra* (chemical inoculation)
SIP	*Aquilaria subintegra* (physical inoculation)
TFC	Total flavonoid content
TPC	Total phenolic content
XRD	X-ray diffraction

LIST OF SYMBOLS

mm y^{-1}	Milimeters per year
I_{corr}	Corrosion current density
E	Potential
E_{corr}	Corrosion potential
β_a	Anodic Tafel slope
β_c	Cathodic Tafel slope
IE %	Inhibition efficiency
ppm	Parts per million
R_{ct}	Charge transfer resistance
C_{dl}	Ideal capacitor
R_s	Solution resistance
Z	Magnitude of impedance
Y_o	CPE coefficient
ω	Angular frequency
j	Imaginary number
f_{max}	Maximum frequency
i_{net}	Net current
$[M-H]^+$	Positive ion mode
m/z	Mass number/charge number
Rt	Retention time
Θ	Surface coverage
K_{ads}	Adsorption equilibrium constant
ΔG_{ads}	Gibbs free energy of adsorption
C	Concentration
Ω cm^2	Ohm's centimeter square

E_r	Antropov's 'rational' potential
E_{pzc}	Potential of PZC
$\bar{I}$	Ionization potential
$\mathcal{A}$	Electron affinity
X	Electronegativity
σ	Global softness
$\mathcal{Y}$	Global hardness
ΔHOMO-LUMO	Energy difference of HOMO and LUMO
Pa	Peak area
consumption %	Consumption percentage
consumption/area	Consumption per area
ρ	Density
A	Area

PERENCATAN KAKISAN BAGI EKSTRAK DAUN *AQUILARIA* METANOLIK BAGI KELULI LEMBUT DALAM LARUTAN ASID HIDROKLORIK

ABSTRAK

Kakisan merupakan salah satu masalah yang memberi kesan negatif kepada banyak industri dan menyebabkan kerugian kewangan kepada industri terlibat. Pelbagai jenis perencat kakisan sintetik telah dibangunkan sebelum ini sebagai langkah mengatasi masalah itu. Namun demikian, perencat kakisan sintetik ini berbahaya kepada kesihatan manusia dan persekitaran. Oleh yang demikian, ekstrak daun *Aquilaria malaccensis* (tanpa inokulasi) dan *Aquilaria subintegra* (tanpa inokulasi, inokulasi dengan bahan kimia, inokulasi secara fizikal) dikaji untuk mewujudkan jenis perencat kakisan yang bersifat mesra alam dan selamat digunakan bagi keluli lembut dalam larutan 1 M HCl. Melalui analisis catur kutub-masa penerbangan kromatografi cecair / spektrometri jisim (Q-TOF LC / MS), kolina, isoleusina, adenosina, fenilalanina dan mangiferin berjaya disahkan hadir. Ekstrak dan sebatian daun tersebut digunakan sebagai perencat kakisan bagi keluli lembut dalam larutan 1 M HCl. Secara keseluruhan, ekstrak daun menunjukkan keberkesananya sebagai perencat kakisan iaitu merencatkan sehingga 96% pada kepekatan 1500 ppm melalui ukuran anti-karat iaitu pengukuran spektroskopi elektrokimia impedans (EIS), pengukuran polarisasi potentiodinamik dan kajian kehilangan berat. Secara keseluruhan, kajian ini mendapati bahawa ekstrak daun *Aquilaria malaccensis* merupakan perencat kakisan terbaik dalam kalangan ekstrak daun yang dikaji. Kajian ini juga menunjukkan bahawa tiada kaitan antara kecekapan perencatan dan cara

perawatan pokok (inokulasi atau tanpa inokulasi). Sebatian piawai didapati mempunyai keupayaan perencatan kakisan yang berbeza dan adenosina didapati sebagai perencat kakisan terbaik dalam kalangan sebatian piawai yang dikaji. Ekstrak daun didapati mematuhi model isoterma penjerapan Langmuir yang diubahsuai di samping menjerap melalui proses penjerapan jenis bercampur yang cenderung kepada penjerapan fizikal. Sebatian piawai didapati mematuhi model isoterma Langmuir, Temkin dan Freundlich serta menjerap melalui pelbagai jenis proses atas permukaan keluli lembut iaitu proses penjerapan jenis fizikal dan proses penjerapan campuran. Analisis kromatografi cecair prestasi tinggi digunakan untuk mengkuantifikasi jumlah adenosina dan mangiferin dan kaedah ini berjaya disahkan bagi tujuan ini. Hasil kajian mendapati bahawa jumlah mangiferin yang wujud semasa pra-kakisan adalah dalam lingkungan 65.16 hingga 86.86 ppm manakala adenosina pula hadir dalam lingkungan 0.32 hingga 0.60 ppm dalam larutan 1000 ppm ekstrak daun. Jumlah adenosina dan mangiferin dianalisis selepas pengukuran anti-karat dan hasilnya didapati bahawa secara am, penggunaan sebatian per luas permukaaan keluli lembut adalah lebih tinggi bagi kaedah elektrokimia berbanding kaedah kajian kehilangan berat. Jumlah penggunaan adenosina tidak bergantung kepada jumlah pra-kakisan adenosina di dalam ekstrak daun 1000 ppm dalam 1 M HCl. Walau bagaimanapun, penggunaan mangiferin bergantung kepada kepekatan ekstrak daun yang digunakan (dalam lingkungan 100 ke 1000 ppm) dalam 1 M HCl. Pemerhatian ini menunjukkan bahawa terdapat penjerapan kompetitif terlibat dalam kalangan sebatian.

CORROSION INHIBITION OF *AQUILARIA* METHANOLIC LEAF EXTRACTS FOR MILD STEEL IN HYDROCHLORIC ACID SOLUTION

ABSTRACT

Corrosion is a problem that negatively affects many industries and causes these industries monetary losses. Many synthetic inhibitors were developed to overcome the corrosion problem. However, these synthetic inhibitors are harmful to human and the environment. In this study, the methanolic leaf extracts of *Aquilaria malaccensis* (non-inoculated) and *Aquilaria subintegra* (non-inoculated, chemical inoculated, physical inoculated) leaf were investigated as green and sustainable corrosion inhibitors for mild steel in 1 M HCl solution. From the quadrupole-time of flight liquid chromatography/mass spectrometry (Q-TOF LC/MS) analysis, choline, isoleucine, adenosine, phenylalanine and mangiferin were confirmed to be present. The leaf extracts and the standard compounds were applied as corrosion inhibitors for mild steel in 1 M HCl solution. Overall, the leaf extracts were shown to have good corrosion inhibition efficiency of up to 96 % at the concentration of 1500 ppm from the anti-corrosion measurements namely the electrochemical impedance spectroscopy (EIS) measurement, the potentiodynamic polarisation measurement and the weight loss study. Among the studied leaf extracts, the leaf extract of *Aquilaria malaccensis* seems to be overall the best as corrosion inhibitor. It was found that there were no relation between the inhibition efficiencies and the treatment of the tree (inoculated or non-inoculated). The standard compounds had various corrosion inhibition abilities and adenosine was found to be the best corrosion inhibitor among the tested standard compounds. The leaf extracts best fitted into the modified Langmuir adsorption

isotherm model and adsorbed by mixed-type but predominantly physisorption process. The standard compounds variously fitted into the Langmuir, Temkin and Freundlich adsorption isotherm models and adsorbed variously onto the surface of the mild steel by physisorption and mixed-type adsorption processes. A high-performance liquid chromatography (HPLC) analysis was applied to quantify the amount of adenosine and the method was successfully validated for this purpose. It was found that the pre-corrosion amount of mangiferin was within the range of 65.16 to 86.86 ppm while adenosine was present within the range of 0.32 to 0.60 ppm in the 1000 ppm leaf extracts. The content of adenosine and mangiferin were analysed for their consumption after the anti-corrosion measurements and it was found that generally, the consumption per area of the surface of mild steel was higher for the electrochemical method than the weight loss study. The total consumption of adenosine was not dependent on the pre-corrosion amount of adenosine in the 1000 ppm leaf extracts in 1 M HCl. However, the consumption of mangiferin was dependent on the concentration of the leaf extract used (range of 100 to 1000 ppm) in 1 M HCl. These suggested that there may be competitive adsorption involved among the compounds.

CHAPTER ONE

INTRODUCTION

1.1 Corrosion of metal

Corrosion of metal is a natural phenomenon which is a gradual attack on the metal, usually as a result of chemical or electrochemical interactions between the metal and the environment. It is not to be confused with the deterioration caused by physical causes as that would be described as erosion, galling or wear. Corrosion is a reaction that causes metals to revert to their original form. This inevitable phenomenon works to a disadvantage to many industries and causes negative impacts. There are several main motivations on the current researches into corrosion which are (Uhlig & Revie, 1985):

- **Economy**

This is a primary motive for many current researches into corrosion as the interest of industries is to maximise profit. The study of corrosion can reduce direct losses and indirect losses due to the problems of corrosion. Examples of direct losses are costs of replacing corroded structures and machineries, and also the labour needed for the replacement of the structures and machineries. Indirect loses are such as the profit lost due to the shutdown of the machinery during the replacement process, loss of products from leaking (corroded) pipelines, contamination of products due to corrosion and loss of efficiency of the machinery.

- **Safety**

As corrosion can affect the quality of the structure of iron and steel, a corroded steel or iron structure is weakened and can be dangerous. Safety is an important consideration for the designing of equipment.

- **Conservation**

The world's supply of iron and steel is limited therefore the effort to conserve iron and steel is important to avoid wastage. Conservation is also important in other related aspects such as water, energy and human effort into the production and fabrication for the iron and steel structures and machineries. It is hard to deny the fact that the supplies will continuously deplete as the demand for the raw materials increase especially with the advancement of technology.

Aside from those factors, corrosion of metals can also be a problem to health, culture and impose technological limitations (Kruger, 2001). According to Kruger (2001), from the viewpoints of health, there is an increase in use of metal prosthetics or implants such as pacemakers, plates and pins. Corrosion remains a problem as they inflame tissues around corrosion products of the implant. From the viewpoints of culture, corrosion accelerates the destruction of artefacts, artistic structures, national landmarks and culturally significant metal structures. With the increase in the pollution incidents, there is a critical concern to conserve structures from the effects of pollution, such as exposure to the acid rain which can corrode the mentioned structures in a long

run. From the viewpoints of technology, a great deal of technology advancement is held back by corrosion, such as geothermal systems that require materials to withstand highly concentrated solutions of corrosive salts at high temperature and pressure. Also there are other difficulties such as with working in the corrosive marine environment.

1.2 Corrosion of iron and coupled electrochemical reactions

Mild steels are useful materials for the construction due to their high flexibility and compressive strength. It is also lighter, more durable and ductile. Due to the high flexibility (low brittleness), mild steels are easier to shape and weld for structural forms compared to other high carbon steels which can break. Additionally, it is also a low cost material. Among the applications of mild steels are everyday objects such as motorcycle frames, automobile chassis and cookware. The study of mild steel in acidic media is important due to its increased industrial applications of acidic solutions such as refining of crude oils. Such works are subjected to strong acid attack on the equipment's surface. Other important fields of application include acid pickling, industrial cleaning, acid descaling, oil-well acid in oil recovery and petrochemical processes. Also, among widely used acids, HCl is the most common (Scattergood, 1987; Amin *et al.*, 2007; Ostovari *et al.*, 2009).

The surface of mild steel that is exposed to the HCl solution without any external influence of electric experiences both the anodic and cathodic reactions simultaneously and freely. At certain sites, the anodic reaction occurs, and passes the electron to other sites where the cathodic reaction can take place (Figure 1.1). The reason that the same surface of mild steel can have both reactions happening simultaneously is due to the

inhomogeneous nature of the surface from impure atoms (other additional elements in the mild steel such as carbon), adsorbed ions from the solution, missing atom from the surface of the mild steel, grain boundaries and other shape differences on the surface of mild steel.

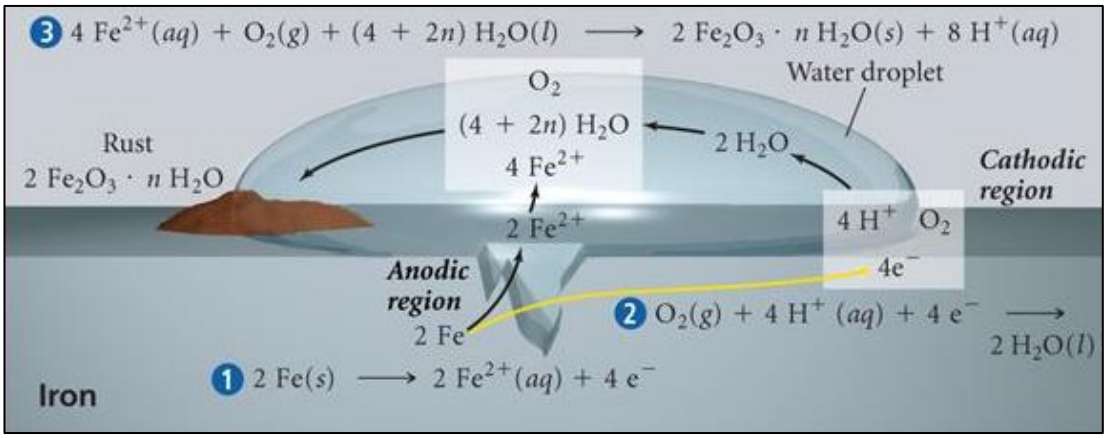

Figure 1.1. Formation of rust, a corrosion product of iron (Tro, 2008)

The main anodic reaction of steel in acidic solution can be summarised as the metal dissolution:

$$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^{-} \quad (E° = -0.45\ V) \qquad (1.1)$$

And the total reaction of iron dissolution in HCl is as such (Groysman, 2009):

$$Fe(s) + 2HCl(aq) \longrightarrow FeCl_2(aq) + H_2(g) \qquad (1.2)$$

For this reaction, the hydrogen gas evolution is observed, indicating it is a prevalently forward reaction.

In water with presence of acid, the cathodic reaction is (Tro, 2008):

$$O_2(g) + 4H^{+}(aq) + 4e^{-} \longrightarrow 2H_2O(l) \quad (E° = 1.23\ V) \qquad (1.3)$$

And the overall reaction is (Tro, 2008):

$$2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2H_2O(l) \quad (E° = 1.68\ V) \quad (1.4)$$

The Fe^{2+} ions then become further oxidized (Tro, 2008):

$$4Fe^{2+}(aq) + O_2(g) + (4+2n)H_2O(l) \longrightarrow 2Fe_2O_3.nH_2O(s) + 8H^+(aq) \quad (1.5)$$

While the resultant Fe_2O_3 product is favoured with the availability of oxygen and water, in the condition of limited dissolved oxygen, Fe^{2+} products such as FeO and Fe_3O_4 (magnetite) are favoured.

While for the cathodic reaction of steel in acidic solution, the possible reactions are (Kruger, 2001):

$$2H^+(aq) + 2e^- \longrightarrow H_2(g) \qquad (E° = 0\ V) \qquad (1.6)$$

and equation (1.3).

1.3 Corrosion inhibitors

Researches are geared towards methods of retarding the corrosion process in the hope of protecting the metal or to the least, prolonging the lifetime of the metal. Modern corrosion science has since begun from the 20th century using the local cell model proposed by U.R. Evans (Evans, 1937; Sato, 2011) and the corrosion potential model proposed by Wagner and Traud (Wagner & Traud, 1938; Sato, 2011). The two models were then joined to describe corrosion as a coupled electrochemical reaction consisting of anodic metal oxidation and cathodic oxidant reduction (Sato, 2011). Currently, there

are many ways to counter the corrosion problem. The methods of corrosion prevention can basically be put as (Chandler & Bayliss, 1985; Fontana & Greene, 1986):

- **Materials selection and design**
- **Protective coatings**
- **Cathodic and anodic protection**
- **Corrosion inhibition**

Among all other methods of corrosion control and prevention, corrosion inhibition is popular due to the ease in application of corrosion inhibitors and the advantage of *in-situ* application without disruption of the process (Koch *et al.*, 2005), aside from being cost effective.

Corrosion inhibitors are substances which when added in small concentrations to the corrosive media will decrease or prevent the reaction of the metal with the media. The main *modus operandi* of organic corrosion inhibitors is the adsorption onto the surface of the metals thus preventing the interaction of the corrosive medium, or the binding with the corrosive species to disable the corrosive species (Ramanathan, 1988; Gentil, 2003; Ju *et al.*, 2008) as adapted by Dariva and Galio (2014) (Dariva & Galio, 2014). The corrosion inhibition can take place by several ways (Dariva & Galio, 2014):

- The inhibitor adsorbs onto the surface to form a protective thin film/ by interaction between inhibitor ions and the surface of metal.
- The inhibitor forms a film by oxide protection of the metal.
- The inhibitor forms a complex with the corrosive component.

Therefore, corrosion inhibitors can be classified into two main groups, inhibitors that inhibit corrosion by forming a protective film over the metal (interference inhibitors) and inhibitors that remove the corrosive species (environmental conditioners). The detailed classification of corrosion inhibitors is shown in Figure 1.2.

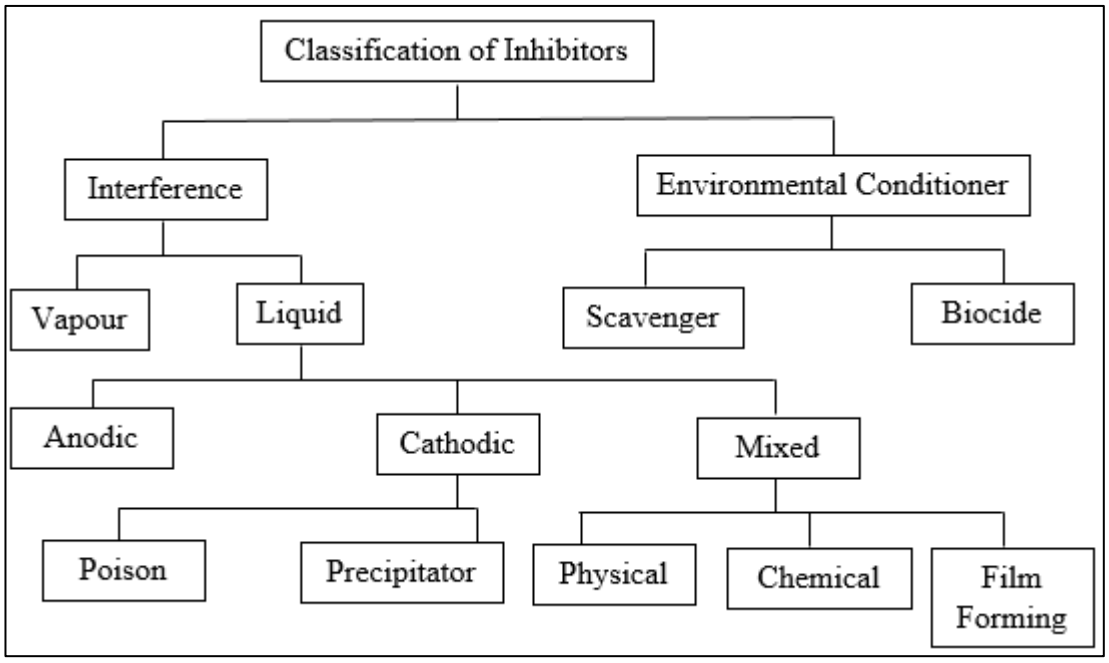

Figure 1.2. Classification of inhibitors (Kruger & Revie, 2000; Ahmad, 2006; Zaferani *et al.*, 2013)

1.4 Natural corrosion inhibitors

There are many organic compounds developed for the purpose of applying them as corrosion inhibitors. Though these synthetic corrosion inhibitors showed good anti-corrosion activity, the issue lies in the toxicity of the said inhibitors towards humans and the environment. Many of these synthetic inhibitors can cause damage, either reversible or irreversible, to the organ system during the process of synthesising the

inhibitors or application (Raja & Sethuraman, 2008). Thus the current trend is to develop corrosion inhibitors that are safe, cost-effective, easily available, environmental-friendly and effective in preventing corrosion. This being so, there have been extensive researches dedicated to the development of corrosion inhibitors that are more environmentally-friendly. The term 'green corrosion inhibitors' becomes a popular term to refer to corrosion inhibitors that are environmentally friendly and/or derived from plant extracts (Kesavan *et al.*, 2012). Some recent examples of corrosion inhibitors that have been studied and reported as green corrosion inhibitors in HCl as a corrosive medium includes *Morus alba* pendula leaves (Jokar *et al.*, 2016), *Strychnos nuxvomica* extract (Soltani *et al.*, 2014), *Melia azedarach* L. seed extract (El-Etre & Ali, 2017) and polysaccharides from *Plantago* (Mobin & Rizvi, 2017).

From the pursuit of discovering more green corrosion inhibitors, currently, many of the inhibitors were naturally derived, especially from waste materials of the plant parts. The development of corrosion inhibitors from waste materials is sustainable as the wastes are being reused instead of being discarded. The waste materials such as fruit peels, seeds and hulls have high antioxidant properties and are rich in phytochemicals that are useful as corrosion inhibitors. Examples of plant waste materials that have shown to have good corrosion inhibition properties are fruit peels extracts (da Rocha *et al.*, 2010), guava seed extract (Kumar *et al.*, 2011), argan hull extract (Afia *et al.*, 2012), garlic peel extract (de Assunção Araújo Pereira *et al.*, 2012) and coconut coir dust extract (Umoren *et al.*, 2012).

Most of the reported plants extracts applied as corrosion inhibitors for mild/carbon steel in 1 M HCl exhibited good inhibition efficiencies up to more than 90 % at low concentration. Some examples include *Justicia gendarussa* extract with up to 93% inhibition efficiency at 150 ppm (Satapathy *et al.*, 2009), *Citrus aurantiifolia* leaves

extracts with up to 97.41 % inhibition efficiency at 2500 ppm (Saratha *et al.*, 2009), *Uncaria gambir* extract with up to 97 % inhibition efficiency at 1000 ppm (Hussin & Kassim, 2011) and *Euphorbia falcata* extract with up to 94.5 % inhibition efficiency at 3000 ppm (El Bribri *et al.*, 2013). In general, the plants extracts contributed to corrosion inhibition due to the presence of many compounds in the extracts that worked synergistically to produce a corrosion retardation effect, as reported by several papers (Avwiri & Igho, 2003; Bouyanzer *et al.*, 2006; Yaro *et al.*, 2013; Deyab, 2015; Odewunmi *et al.*, 2015). Mostly, the corrosion inhibition effect was believed to be actively contributed by the compounds that belong to the phytochemical groups which are also good antioxidants such as alkaloids, flavonoids, and tannins (M'hiri *et al.*, 2016). Extensive studies on known molecules have been done and it was reported in many papers that inhibitor molecules with the presence of bond-forming, electron-rich groups/atoms are known to be responsible for the corrosion inhibition properties (Morales-Gil *et al.*, 2004; Şafak *et al.*, 2012; Ansari *et al.*, 2014; Hamani *et al.*, 2014). The widely accepted explanation of corrosion inhibition by these plant extracts is the adsorption of the inhibitors' molecules on the surface of a metal forming a barrier between the metal and corrosive substance, thus preventing corrosion (Wahdan *et al.*, 2002; Benabdellah *et al.*, 2006; Hamdy & El-Gendy, 2013; Rajeswari *et al.*, 2014; Zhang *et al.*, 2015).

1.5 Agarwood trees

Agarwood, or also known as aloeswood, eaglewood, karas, gaharu, oud and other names is the resinous heartwood produced by several types of *Aquilaria*, *Gonystylus*

and *Gyrinops* trees. In Malaysia, the common species are *Aquilaria hirta*, *Aquilaria malaccensis* and *Aquilaria rostata* (Barden *et al.*, 2000). *Aquilaria* species has adapted to live in various habitats including areas that are rocky, sandy, well-drained slopes, ridges and land near swamps. They typically grow in locations with average daily temperatures of 293 to 295 K (Kessler & Sidiyasa, 1994; Afifi, 1995; Wiriadinata, 1995).

Agarwood is a highly sought after resinous product of the agarwood trees due to the highly valuable and distinctive fragrance of the resin which fetches very high prices when sold. If sold after the resin is processed and extracted to obtain the agarwood oil, the pure agarwood essential oil has a high value of up to 30 thousand US dollars per kilogram in year 1999 (Barden *et al.*, 2000). According to an article published in 2017, prices offered for raw agarwood can fetch RM 2000 per kg for the first grade (Kanazawa, 2017). Aside from being traded as oil forms, international trades in agarwood involves wood, wood chips, powder and also finished products such as perfumes, incense and medicine. Its medicinal usage dates as far back as a few thousand years ago, referencing from Ayurvedic medical texts and agarwood continues to be used inclusive of Malaysian, Tibetan and traditional East Asian medicines (Barden *et al.*, 2000). The purported benefits of agarwood include treatments as mainly anti-inflammatory and related activities (Hashim *et al.*, 2016) such as pain reliever, asthma reliever, rheumatism, tonic during pregnancy, after childbirth and for diseases of female genital organs. Large agarwood branches or trunks (weighing more than 10 – 20 kg) are usually bought by customers from Japan for religious uses (Barden *et al.*, 2000). Smaller quantities of agarwood are also used for carvings.

Recent reported works regarding agarwood are focused on several aspects including inoculation techniques for producing agarwood resin or volatile compounds (Monggoot *et al.*, 2017), discovery of new compounds from agarwood trees (Li *et al.*, 2016; Yang *et al.*, 2017), analytical methods to grade the agarwood resin (Pasaribu *et al.*, 2016) and to profile the fungus-plant interaction (Wong *et al.*, 2015), and methods to distinguish fake and pure agarwood (Lias *et al.*, 2016). A review in 2016 by Hashim *et al.* (2016) lists the major compounds found in the plant material (can be from the leaf, stem, trunk, fruits, etc) of *Aquilaria* species and are shown in Figure 1.3.

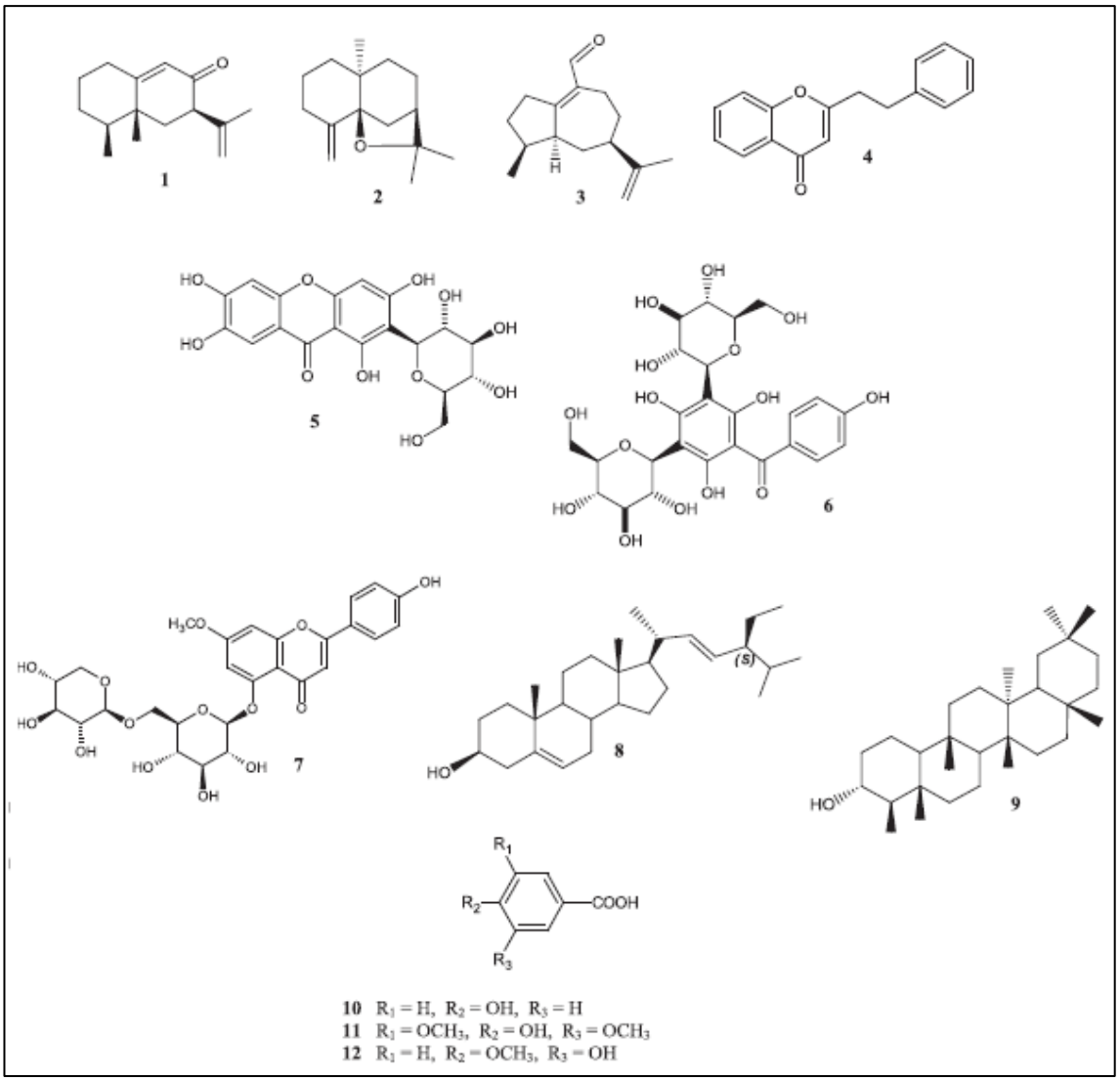

Figure 1.3. Chemical structures of the major compounds found in agarwood plant materials: neopetasane (eremophilane) (1), β-agarofuran (2), (-)-guaia-1(10),11-dien-15-al (3), 2-(2-phenylethyl)chromone (4), mangiferin (5), iriflophenone 3,5-C-β-diglucoside (6), genkwanin.5-O-β-primeveroside (7), stigmasterol (8), 3b-friedelanol (9), 4-hydroxybenzoic acid (10), syringic acid (11) and isovanillic acid (12) (Hashim *et al.*, 2016)

1.5.1 *Aquilaria malaccensis*

Aquilaria malaccensis (Latin word for from Malacca, a place in Malaysia) (Figure 1.4) is from the *Thymelaeaceae* family and it is a type of agarwood producing tree. The

tree is a large evergreen tree growing over 15 to 30 m tall and 1.5 to 2.4 m in diameter with white flowers (Barden *et al.*, 2000).

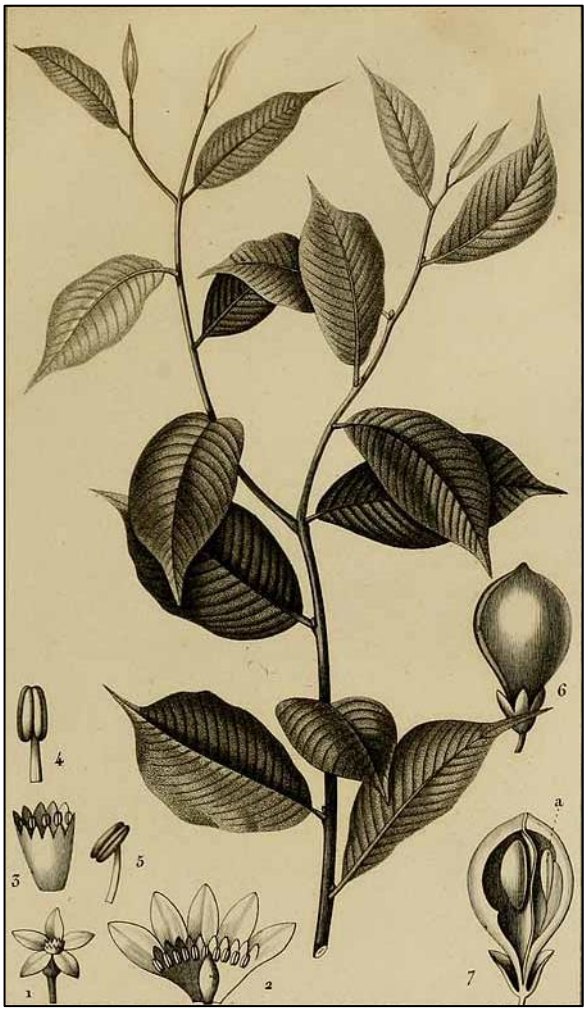

Figure 1.4. *Aquilaria malaccensis* illustration by P.J. F. Turpin (Turpin, 1985)

The leaf is described to grow alternately with a petiole of 4-6 mm long, shiny on both sides curving upwards to the margin with veins of 12 to 16 pairs, of elliptical oblong to oblong lanceolate shape of the size 7.5 to 12 × 2.5 to 5.5 cm (Oyen & Dung, 1999). The capsule shape is obovoid or obovoid oblong with a cuneate capsule base and it has round capsule apex. The calyx lobe is ovate-oblong at 2 to 3 mm long that is spreading

or reflexed with a calyx tube that is bell-shaped. The flower length is 2.5 cm (Mohamed, 2016). *Aquilaria malaccensis* trees are widely distributed in South and South-East Asia. It is found in Bangladesh, Bhutan, Iran, Indonesia, Malaysia, Myanmar, Philippines, Singapore and Thailand (Dariva & Galio, 2014).

1.5.2 *Aquilaria subintegra*

Aquilaria subintegra (Figure 1.5) is from the Thymelaeaceae family and it is a type of agarwood producing tree. The tree is a size of a shrub.

Figure 1.5. Photo of leaf (left) and fruit (right) of *Aquilaria subintegra* ("Agarwood Type," 2014)

The leaf shape is described as elliptic-oblong or slightly obovate-oblong and the texture is described as papery but almost smooth. The capsule shape is ellipsoid oblong with a cuneate capsule base and it has round capsule apex. The calyx lobe is ovate-oblong at 3.5 to 5 mm long and the calyx tube is bell-shaped. The flower length is 0.75

to 1.1 cm. *Aquilaria subintegra* is known to be distributed in Thailand (Mohamed, 2016).

1.6 Agarwood leaf

While the agarwood resin gains much attention, the agarwood leaf was not as popularly researched on, probably due to the drastically lesser market value of the leaf in comparison to the resin and woody parts of the tree. Current researches about the agarwood leaf are focused on profiling and discovering the chemical properties and expanding the application of the leaf derivatives in various fields. As the agarwood development could be only at the core of the woody parts and thus concealed from the outside, when agarwood is harvested, usually, the whole tree is uprooted and the woody parts such as the trunk, branches and roots are split open to look for the infected heartwood. Considering the fact that there are tens of thousands of *Aquilaria* trees harvested annually for the production of agarwood oil (Soehartono *et al.*, 2002), there would be a large amount of leaf produced. The leaf was not useful for the extraction of the resin and it would largely be a waste that needs to be disposed. If the leaf waste are not properly managed, it could lead to pollution and other disposal problems. Thus, it would be an environmentally-friendlier step to make use of the leaf as it can provide as a sustainable resource when developed into useful products from the abundant leaf which would otherwise be thrown away or even disposed by burning.

The leaf was traditionally used as teas for stomach ailments and was believed to help with many other ailments. The leaf is believed to contain high antioxidant properties that could be beneficial for the health of the consumers. In reported papers, the

agarwood leaf was tested for its benefits in laxatives effect (Hara *et al.*, 2008), for antihyperglycemic effect using rats (Pranakhon *et al.*, 2011), antipyretic, analgesic and anti-oxidative effects in rodents (Sattayasai *et al.*, 2012) and hepatoprotective activity (Rahman *et al.*, 2013).

Aside from the researches into the applications of the agarwood leaf, there were also reports on the chemical constituents present in the agarwood leaf. An antioxidant properties studies of the leaf of *Aquilaria malaccensis* supported the fact that the leaf is rich in antioxidant with several phytochemicals screened such as tannins, flavonoids, saponins and alkaloids, in that methanolic extract of the leaf (Huda *et al.*, 2009). There were many identified compounds that can be summarised to come from various groups such as phenolic acids, benzophenones, xanthonoids, flavonoids, terpenoids, steroids, fatty acids and carbohydrates (Hashim *et al.*, 2016). From the same review publication by Hashim *et al.* (2016), most of the identified compounds were from the benzophenones and flavonoids groups. From the benzophenones, xanthonoid and flavonoids groups, most of the compounds identified are glucosides such as mangiferin and its related species and iriflophenone related species. Since good inhibitors have functional groups that enhances adsorption such as –OH group, N, O and P atoms and π-bonds which are present in most phytochemical groups and antioxidant rich compounds, the richness of antioxidants and useful phytochemicals (such as the phenolic compounds) in the agarwood leaf extracts could suggest that the leaf extracts could potentially be applied as a corrosion inhibitor.

As mentioned, the agarwood tree leaf was paid less attention compared to the agarwood resin and its products, hence reports on works to do with agarwood leaf are also more limited in comparison to the agarwood resins and its products. Recent reported works regarding agarwood leaf are focused on several aspects including

identification of compounds from agarwood leaf (Lee *et al.*, 2016), chemical properties of the leaf (Hendra *et al.*, 2016) and pharmacology usage discovery/application of the leaf (Alam *et al.*, 2017; Supasuteekul *et al.*, 2017). The application of agarwood leaf as corrosion inhibitors were relatively unreported.

1.7 Inoculation on agarwood trees

Aside from the factor that the distinct fragrance of the agarwood is difficult to replicate synthetically, the high price of the agarwood is also due to the formation of agarwood itself being not a guaranteed occurrence in every *Aquilaria* and *Gyrinops* (another type of agarwood producing tree) tree especially in the wild. As agarwood is only formed as a self-defense mechanism by the tree, the formation of agarwood is usually due to wounding or pathological processes, but these processes of the agarwood formation are poorly understood and remain for most part a mystery. The highest grades of agarwood are usually produced in wild, however, it is estimated that only 10 % of the wild *Aquilaria spp.* produces agarwood resin (Barden *et al.*, 2000). In the wild, the agarwood can be formed when animals such as wild boars graze and scratch on the agarwood trunk, insects such as snails and ants hatching a nest in the trunk and a dying agarwood tree, among other possible methods. The quality of the agarwood produced is also dependent on other factors such as the age of the tree, seasonal, environmental and genetic variation.

Due to its rarity but immense demand for agarwood for various purposes, to increase the supply of agarwood, the trees were farmed and induced by inoculation methods to produce the resin. Inoculation methods are aimed to cause the agarwood production in

the trees by artificially stimulating the self-defense mechanism of the tree. The inoculation methods basically involves penetration techniques and/or insertion of microbial concoctions to create stress to encourage the formation of resin. Some examples of inoculation include methods such as described in Figure 1.6.

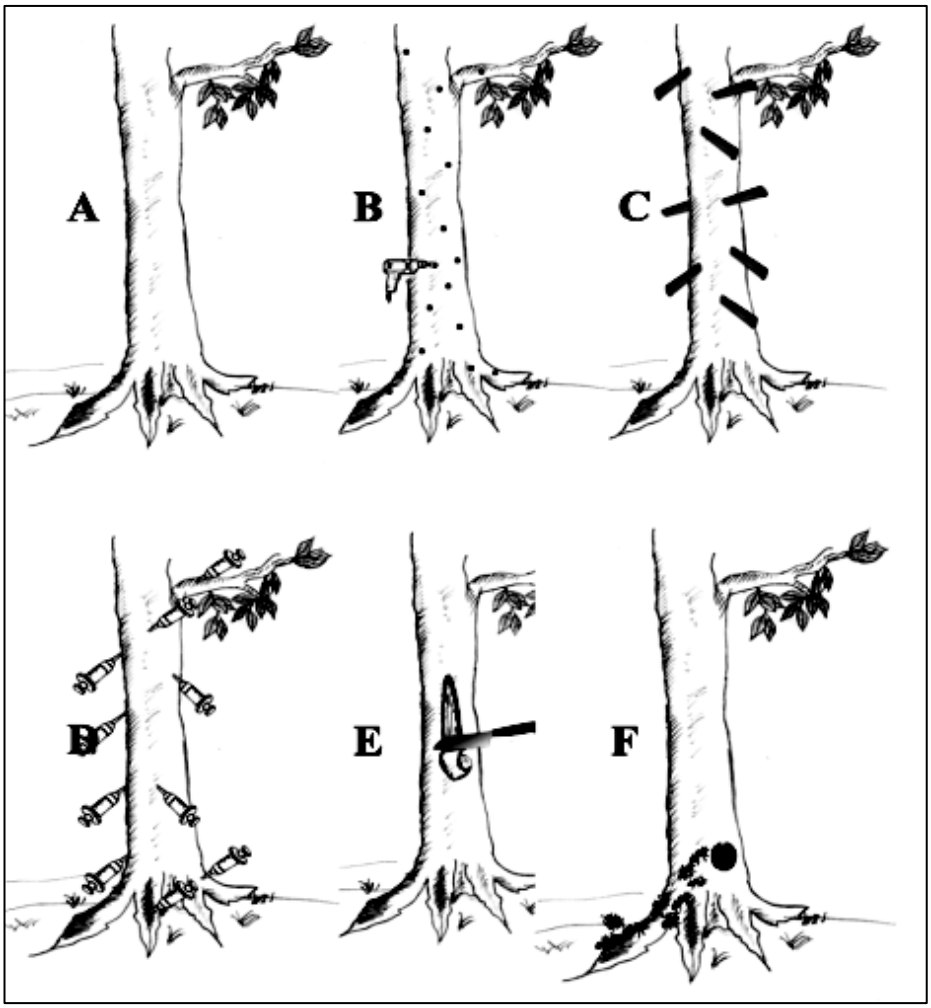

Figure 1.6. Illustration of induction methods commonly used in agarwood formation: (A) no induction/injury made for natural maturation process, (B) drilling the stems, roots and large branches, (C) Installation of foreign objects (metal, PVC) into pores, (D) inserting syringes, (E) peeling off the barks and (F) digging a hole to facilitate hatching of ants and snails in the tree (Akter *et al.*, 2013)

The inoculation process stimulates the self-defence mechanism of the tree and from several reports, the type of inoculation process can cause the composition of the oils to be different from one another. A paper reports on the effect of the type of inoculation treatment on the sesquiterpene and oil content. From the paper, it was reported that after one year of the inoculation treatment on *Aquilaria crassna,* the sesquiterpene content was the highest in the chemically treated (mixture of acid sulfuric and sodium methyl bisulfate) tree, followed by mechanical treatment (nail hammering) and control (no treatment) tree. The oil content was in a reverse trend with the control and mechanical treatment yielding more oil than the chemical treatment. Two years after treatment, the control tree had the lowest sequiterpene level while the biological treatment (mixture of fungi) yielded the highest sesquiterpene content (Van Do *et al.*, 2015). The composition of oil obtained from healthy, naturally infected and inoculated *Aquilaria agallocha* was studied in another paper and it was found that the oil content of the naturally infected tree was different from the oil content of the other trees (Tamuli *et al.,* 2005). Another paper reported the biochemical changes in *Aquilaria malaccensis* Lamk. for healthy, naturally infected and pathogen inoculated trees. It was found that the protein, sugar, ascorbic acid and phenol content of the healthy plant increased during incubation from 10 to 40 days while the protein, sugar, ascorbic acid and phenol content for the naturally infected and pathogen inoculated plant decreased during incubation (Tamuli *et al.*, 2014). From the same paper, several possible explanations were provided for the observed changes during incubation for the healthy and infected plants. The decreased sugar levels in diseased plants can be caused by respiration or utilisation of sugar by the fungi for the purpose of the fungi's own growth (Nema, 1989) or the breakdown of carbohydrate by the fungi's enzyme (Prasad *et al.*, 1988). The decrease in ascorbic acid may be caused by fungus activity or host-

pathogen complex as it was reported that the ascorbic acid level in lime fruits decreased in infected fruits (Reddy *et al.*, 1984). The decreased phenolic content may be caused by the inability of the diseased plant from producing phenolic compounds or may be associated with the susceptibility of the plants invaded by pathogen (Khatri *et al.*, 1985; Nema, 1989). The decrease in protein in infected plant could be due to the degradation of proteins by the proteolytic enzymes secreted by the pathogens (Tamuli *et al.*, 2014).

Considering the reports on the differences of chemical content (sesquiterpene content, oil content, sugar, protein, ascorbic acid and phenolic content) due to the different types of inoculation method or the differences between the healthy tree and naturally infected tree, the agarwood leaf extracts can be analysed for the effects of the different treatments to the agarwood tree from the viewpoint of anti-corrosion analysis for mild steel in hydrochloric acid solution.

1.8 Corrosion evaluation methods

For the purpose of evaluating the agarwood leaf extracts as corrosion inhibitors, several corrosion evaluation methods can be employed. Most of the reported plants extracts were evaluated for their anti-corrosion properties using similar methods used in this thesis. The anti-corrosion measurements employed for this study to evaluate the anti-corrosion properties of the agarwood leaf can be categorised as the electrochemical methods and the gravimetric method (weight loss study). Each of these methods contributes different information on the anti-corrosion behaviour of the inhibitors and all are important for collectively describing the anti-corrosion behaviour

of the inhibitor from the point of view of corrosion as an electrochemical process (from the electrochemical methods) and for the corrosion process observed as a natural and gradual process (from the weight loss study).

1.8.1 Electrochemical methods

As the corrosion process is an electrochemical reaction, the anti-corrosion measurement can be observed from the viewpoints of electrical activities. Thus, the electrochemical methods offer more information for understanding the anti-corrosion process as an electrochemical process. Aside from this, the electrochemical methods are a faster technique to measure corrosion compared to the weight loss study which could take up to weeks or months to complete, especially for metal specimens that are resistant to corrosion. The typical setup for an electrochemical method is shown as Figure 1.7.

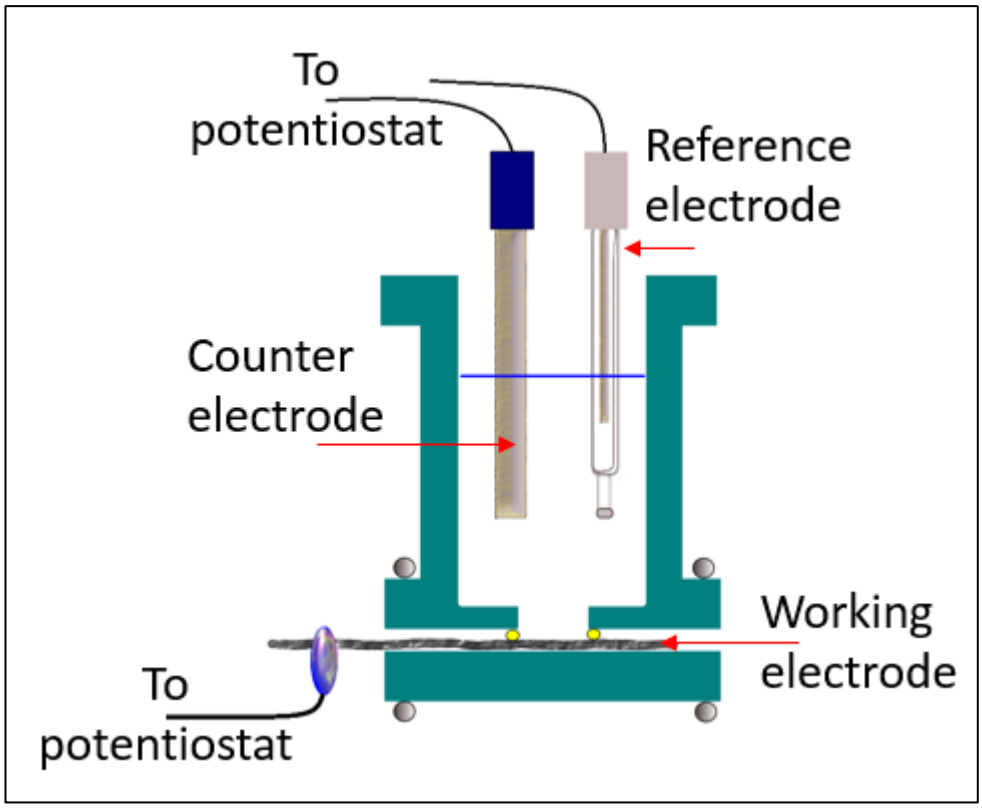

Figure 1.7. Electrochemical cell setup

A cell for the electrochemical analysis consists of a working electrode (metal specimen), a reference electrode, a counter electrode, corrosive medium with/without the inhibitor and a potentiostat connected to the computer. The conditions of the electrical influence can be controlled by the computer and executed by the potentiostat. A successful corrosion inhibition by the corrosive medium containing the inhibitor will have a higher resistance (for the EIS measurement) and lower corrosion current density (for the potentiodynamic polarisation) than the specimen analysed in the corrosive medium only (blank).

1.8.1(a) Electrochemical impedance spectroscopy (EIS) analysis

Dielectric spectroscopy/Alternating current (AC) impedance spectroscopy/electrochemical impedance spectroscopy (EIS) is a commonly used method for the purpose of corrosion evaluations. This method has the advantage of being a rapid and non-destructive technique. It is also a useful technique for analysing solutions with lower conductivity and high resistance coating (Revie & Uhlig, 2008). As the name suggests, an AC impedance measurement is a determination of electrical impedance of the metal specimen to electrolyte interface at various alternating current (AC) frequencies (Schweitzer, 2006). A low amplitude AC wave is imposed on a potential, usually the resting potential of the cell, for this technique. All three components of resistance, capacitance and inductance result in the blockage of current flow:

$$E=IZ \tag{1.7}$$

where E is the potential (V), I is the current (A) and Z is the magnitude of impedance containing elements of an equivalent circuit (for example; capacitor and inductor).

The impedance measurement is made of the imaginary component (resistance) and the real component (capacitance and inductance). A result of such measurement is the Nyquist plot or the Bodes plot, both of which represents the same result in a different perspective: the correlation of the imaginary impedance to the real impedance (Nyquist) or the correlation of the impedance magnitude to log frequency and phase angle (Bodes).

The shape of the Nyquist plot can be fitted into equivalent circuits to further describe the mechanism of the reaction. Components such as the ideal capacitor (C_{dl}), solution resistance (R_s) and charge transfer resistance (R_{ct}) were used to build an equivalent circuit that best fits the shape of the Nyquist plot obtained from the corrosion analysis. An example of Nyquist plot and its component is shown in Figure 1.8.

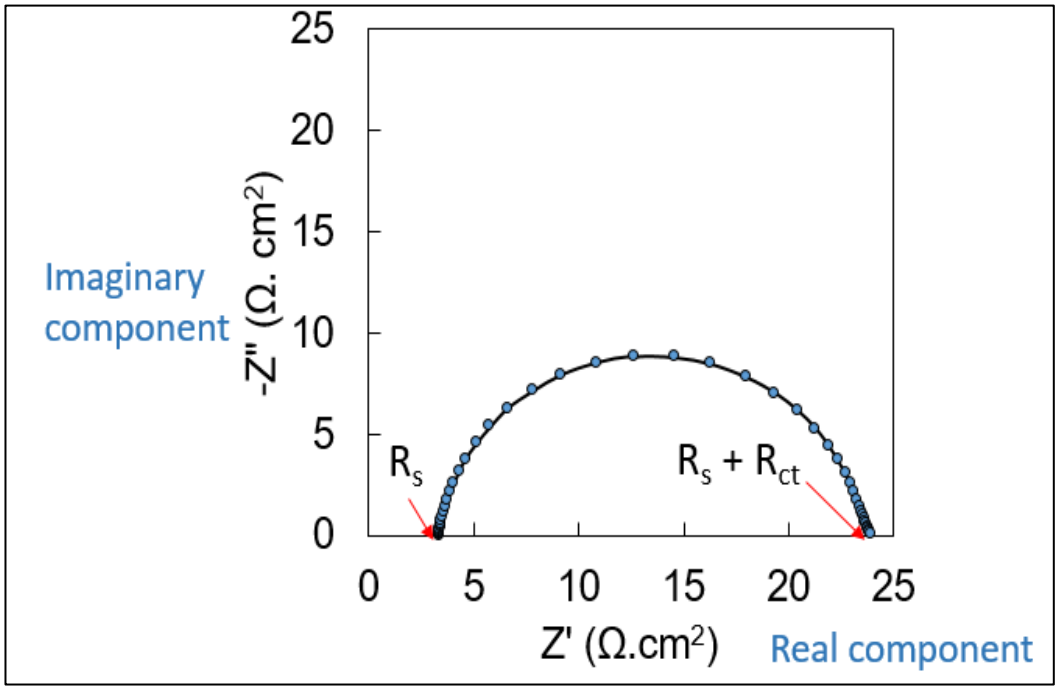

Figure 1.8. An example of a Nyquist plot

The constant phase element (CPE) describes the behavior of the electric double-layer when the impedance of the double layer does not behave like the ideal capacitor. The impedance of CPE can be described by the following equation:

$$Z_{CPE} = Y_o^{-1}(j\omega)^{-n} \quad (1.8)$$

where Y_o is the CPE coefficient, ω is the angular frequency, j is the imaginary number and n is the CPE exponent related to the phase shift.

A Bodes plot typically consist of the Bode magnitude plot (impedance magnitude versus log frequency) and the Bode phase plot (phase angle versus log frequency).